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ZINC SORPTION BY SELECETED SOILS IN TOSHKA REGION

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ABSTRACT: *Fifteen surface soil samples were selected from various locations in Toshka region according to their in $CaCO_3$ and clay content, to study the adsorption of Zn by these virgin soils .*

Zn adsorption data were in harmony with Langmuir isotherm equation, specially at low Zn concentrations less than 10 ug Zn ml^{-1} .

The maximum adsorption values were ranged between 0.278 and 0.969 mg g^{-1} soil, and correlated closely with total clay and clay content as a mineral , while insignificant positive linear relationship between Zn and $CaCO_3$% in the clay fraction was resulted .The later finding may be means that $CaCO_3$ in the very fine fraction , exhibited surface reaction and reduced Zn availability , but its values were not statistically enough to be significant. The values of bonding energy were ranged between 0.010 and 0.216 L mg^{-1} soil.

Keywords *: Calcareous soil – Zinc – Sorption – Adsorption isotherm – Bonding energy – Langmuir equation.*

INTRODUCTION

Toshka region is bounded by longitudes 30° 30˙ and 32° 00˙ east and latitude 22° 23˙ north (Said , 1962) . In this region work is under way to extend the Nile water into the heart of the western desert to the Dakhela and Khrga oases.This bold project would create in effect a new agricultural land and was decided as the national project for the twenty first century (Egyptian Ministry of Economy, Dec. 1998).

Zinc is an essential mircronutrient for human, animals and higher plants (Kiekens,1999). Zn conentration in soil solution and its availability to crops is controlled by sorption - desorption reactions at the surfaces of soil colloidal materials (Swift and Mclaren, 1991). Sorption of Zn is mainly depends on the soil characteristics, particularly pH, cation exchange capacity (CEC), the nature and content of clay, different oxides of Fe, Al and Mn as well as $CaCO_3$ (El Gabaly,1990; Misra and Tiwari,1966; Naidu and Harter, 1998 and Harter and Naidu, 2001).

Traditioally, the adsorption of ions by soils has been quantitively calculated by the Langmuir isotherm equation.

The aim of this work, is to study Zn adsorption on the solid phase of Toshka soils using the Langmuir isotherm equation.

MATERIALS AND METHODS

Fifteen surface soil samples (0 – 30 cm. depth) were selected from Toshka region, to represent the calcareous soils at that area (Fig.1). Samples were air dried, ground by wooden pestle and sieved through nylon sieve and their main physical and chemical properties were determined using the standard procedures,as described by Black (1965) and Jackson (1973) , the obtained results are given in (Table 1).

Triplicates of the 0.5 g from each soil was placed in Polyethlene centrifuge tubes (100 ml capacity) equilibrated with 50 ml solution containing 8 levels of Zn (0.0 , 2.5, 5.0 , 7.5 10.0 , 15.0 , 20.0 and 30.0 mg g^{-1} soil) as $ZnSO_4.7H_2O$. Each Zn solution was initially adjusted to pH 7, and 2 drops of tolune was added. Equilibration was achived by using roatory shaker at 5.0 h. intervals for a period of 48 h. at room temperature ($27 \pm 1°C$). The contents were then centerifuged and the Zn- concentration in the supernatant solution were determined using atomic absorption spectrometry. The adsorbed amount of metal was calculated from the different between the initial conentration and the final equilibrating metal concentration (Mandal et al., 2000). The result of the blank(O mg g^{-1} Zn)treatment was always taken into considration . Zn concentration in the supernatant was determined and the obtained data were fitted to linear form of Langmuir equation :

$$C/x/m = 1/kb + C/b$$

Where : C is the equilibrum Zn–concentration in solution (mg L^{-1}) , X/m is the amount of adsorbed Zn as (mg g^{-1} soil), K is a constant related to the bonding energy of soil for Zn and b is a constant related to adsorption maximum (mg g^{-1} soil).

Correlation coefficients between C and C/x/m were calculated and lines fitted by regression analysis. Slope and intercepts of lines were used to calculate adsorption maximum and bonding energy contents(Rahmou et al., 2006).The statistical analysis was carried out according to (Snedecor and Cochran, 1981).

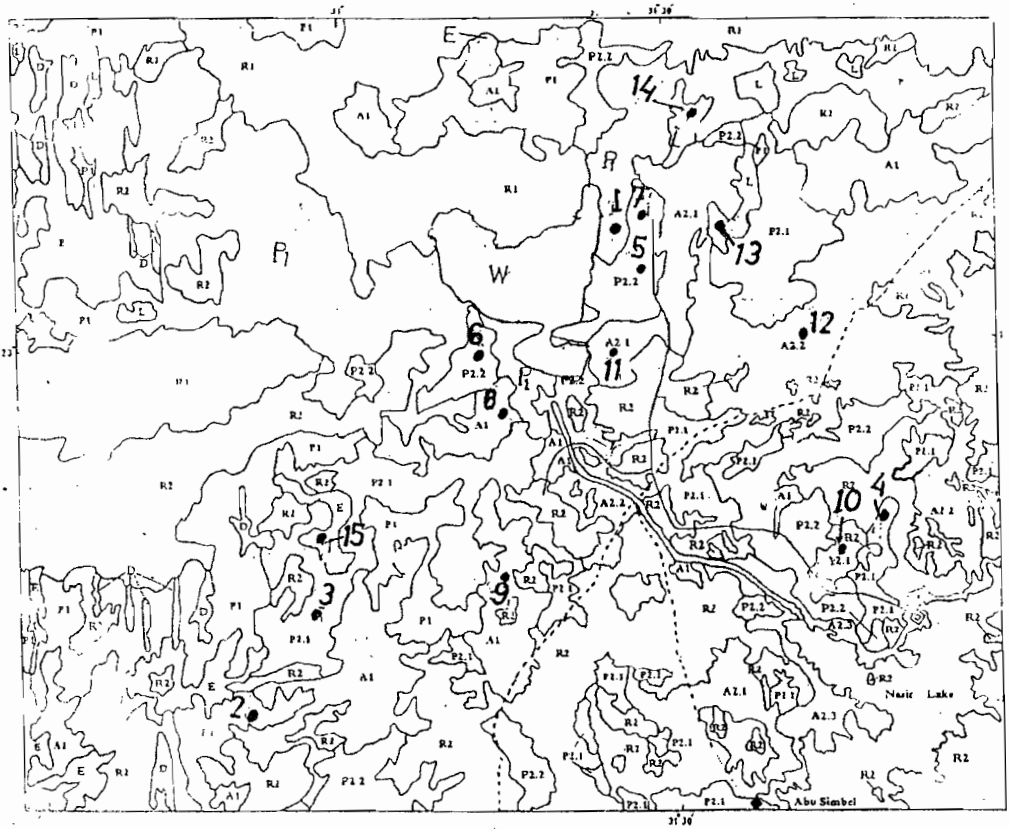


Fig (1): Locations of the studied soil samples.

- Physiographic soil legend:
  - P_1 → Pediplain of soft rock (shale)
  - A_1 → Alluvial deposits over soft rock suprolite
  - A_2 → Alluvial deposits over hard rock (sandstone) suprolite
  - L → Playa
  - E → Aeolian plain
- Miscelianeous land types and cover:
  - R_1 → Dissected questa.
  - R_2 → Rock land.
  - D → Barchan sand dunes
  - W → Seeped water body with changeable beach line.

Table (1):Some physical and chemical properties of the initial soil sample.

Soil sample No.	Clay fraction (%)	Clay as Mineral (%)	$CaCO_3$ in the clay fraction	pH soil paste	O.M (%)	$CaCO_3$ (%)	EC_e (dS/m)	CEC (mq 100^{-1} g soil)
1	10.8	5.2	5.6	7.8	0.02	16.0	4.4	8.7
2	7.4	5.2	2.2	7.9	0.07	12.1	6.8	8.2
3	10.7	9.8	0.8	7.7	0.12	13.5	6.0	8.5
4	14.0	12.6	1.5	7.8	0.02	20.3	4.8	15.1
5	15.2	12.8	2.4	7.8	0.17	16.0	4.4	16.4
6	17.2	15.6	2.4	7.6	0.07	26.0	18.0	18.4
7	26.9	18.7	8.2	7.8	0.29	19.4	15.3	29.3
8	15.4	12.8	2.6	7.7	0.14	12.3	20.6	16.4
9	7.6	6.6	1.1	7.8	0.10	17.0	2.2	8.2
10	11.0	9.2	1.8	7.2	0.15	13.1	67.3	11.8
11	8.2	7.3	0.9	7.8	0.01	15.5	1.8	3.9
12	50.6	48.8	1.8	7.9	0.12	13.1	7.4	54.0
13	6.7	5.6	1.2	7.6	0.06	17.5	10.1	7.3
14	7.2	5.6	1.6	8.1	0.02	12.8	1.8	5.8
15	29.6	27.8	1.8	7.5	0.23	14.9	9.8	32.1
Mean	15.9	13.57	2.4	7.3	0.01	15.97	12.0	16.3

RESULTS AND DISCUSSION

1- Soil properties :

Data in (Table 1) showed that soils under study are sandy in texture , mildy alkaline in reaction (mean = 7. 3), and the values of electric conductivity (EC_e) being in the range of 1.8 to 67.3 , while the mean value was 12.0 dS/m . Data also showed that these soils are very poor in organic matter content with a mean value 0.01%, the negligible amounts of organic matter are mainly due to the dryness and hot climate effect (Serry *et al.,* 1966; Moustafa et al., 1988 and Hassanein *et al.,* 2002). As for calcium carbonate, the obtained data resulted that its values ranged between 12.1 and 26.0 %, therefore these soils could be considered calcareous in nature according to the definition of (Anter *et al.,* 1973) . in addition , cation exchange capacity (CEC) ranged between 3.9 and 54.0 mq 100^{-1} g soil , with a mean value 16.3 mq 100^{-1}g soil.

2- Langmuir adsorption equation :

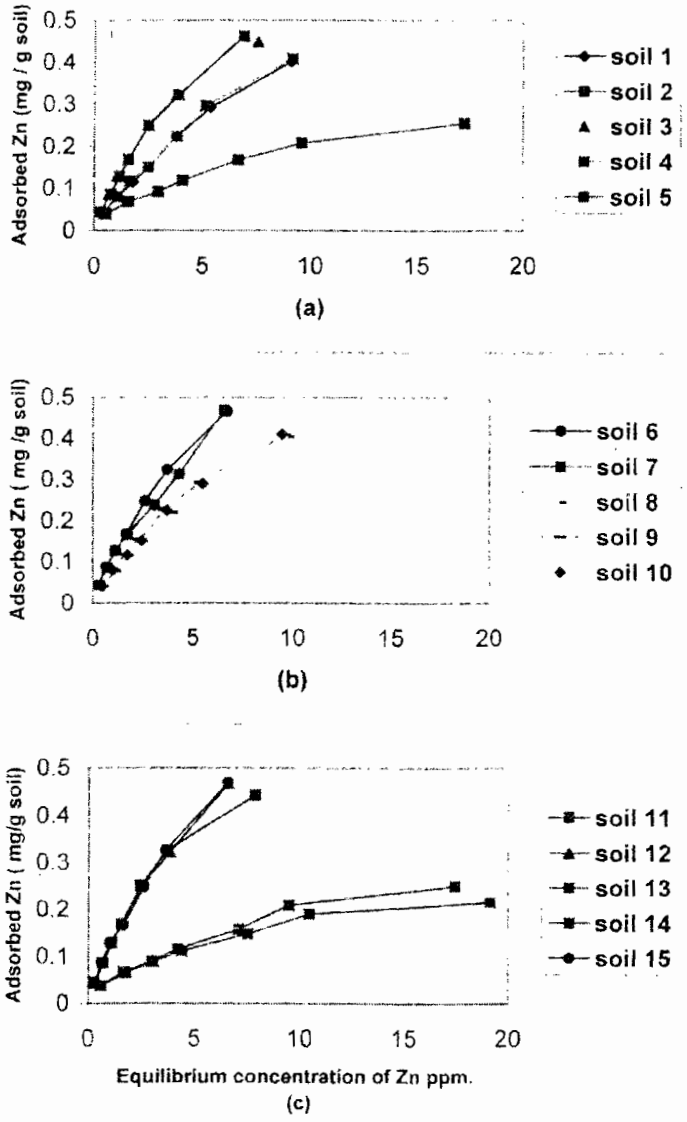
The resulting curves of plotting the adsorbed Zn (mg/g soil) versus Zn equilibrium concentration(ppm)illustrated in(Figs 2–a,b,c).Zn adsorption isotherm showed favorable agreement with Langmuir isotherm curve for all soils, especially at low Zn concentration(< 10 mg g^{-1}). Similar data were obtained on alluvial soil by Rahmou *et al.*, (2006). El-kouny (2004) argued that calcareous soil absorbed more amounts of Zn than alluvial soil and this could be due to the presences of higher sorption sites for Zn. Pulford (1986) reported that Zn reactions with soil involve both surface adsorption and a perception mechanisms. The highest sorption of Zn by the soils under study may be return to Zn co-perception with carbonate of soil (Jurinake and Bauer, 1956 and El-kouny, 2004).

3- Constants of Langmuir equation :

Table (2) showed that the calculated adsorption maximum (b), the relative bonding energy (K) and the linear equations for the studied soils. The Zn adsorption maximum ranged between 0.278 and 0.969 mg Zn g^{-1} soil. The obtained values of constant K (bonding energy) ranged between 0.010 to 0.216 L mg^{-1} soil.

Table (2): Constant and linear equations derived from the Langmuir equation.

Soil sample No.	The linear Langmuir equation C/x/m=1/kb+c/b	Bonding energy (k) L mg^{-1} soil	Adsorption maximum (b) mg Zn g^{-1} soil	Coefficient of determination (r)
1	C/x/m=11.742+1.4109x	0.120	0.709	0.96**
2	C/x/m=19.257+2.888x	0.150	0.346	0.97**
3	C/x/m=6.8554+1.319x	0.192	0.758	0.99**
4	C/x/m=12.299+1.1587x	0.094	0.863	0.95**
5	C/x/m=7.2733+1.151x	0.158	0.869	0.96**
6	C/x/m=7.1941+1.1281x	0.157	0.886	0.91**
7	C/x/m=7.8859+1.225x	0.155	0.891	0.92**
8	C/x/m=12.814+1.1456x	0.089	0.873	0.98**
9	C/x/m=11.916+1.1889x	0.010	0.841	0.99**
10	C/x/m=11.915+1.225x	0.103	0.816	0.97**
11	C/x/m=6.5356+1.4143x	0.216	0.707	0.98**
12	C/x/m=7.4849+1.0319x	0.138	0.969	0.98**
13	C/x/m=20.213+3.5925x	0.178	0.278	0.98**



Figs. (2-a,b,c) Effect of added Zn on Zn-adsorption by soil samples.

4- Relationship between Zn adsorption maximum and the effective soil characteristics:

Zn adsorption depends on the soil characteristics, particularly pH, cation exchange capacity (CEC) , the nature and content of clay and different oxides of Fe, Al and Mn as well as $CaCO_3$ (Harter, 1991 and Hazra and Mandal, 1996). The relation between maximum adsorption and some soil properties i.e. (a) CEC mq 100^{-1}g soil , (b) EC_e dSm^{-1} (c) O.M % (d) the total percentage of $CaCO_3$ and (e) the pH were statistically calculated and their coefficients are listed respectively as following : (a) r =0.609* (b) r = 0.226 (c) r = 0.475 (d) r = 0.244 (e) r = 0.298 .

The former date (Figs 3-a,b,c,d) clearly showed that the correlations between the aforementioned soil characteristics and maximum adsorption were positive and significant for CEC, while EC, O.M, and $CaCO_4$ exhibited insignificant positive relations. On the contrary , no obvious relation was resulted between, pH values and Zn adsorption, in spit of , the enhancing effect of high pH values on Zn retention as found and recorded by several workers e.g. Jurinake and Bauer, 1956; Randhawa and Broodbent (1964); Harter, (1983); Boekhdd et al., (1993) and Harter and Naidu, (2001) the interpretation of that result may be return to the semi quall pH values of the investigated soils, in which the mean = 7.5 . Regarding other soil properties Kabata– Pendians and Pendias 1992;Shuman (1980 & 1997) and Naidu and Harter (1998) , climed that O.M can be a very important factor in Zn sorption by the soil. But as shown in the previous result insignificant positive relationship was resulted between Zn adsorption and O.M, and this may be due to the Bonding energy of the investigated soils.

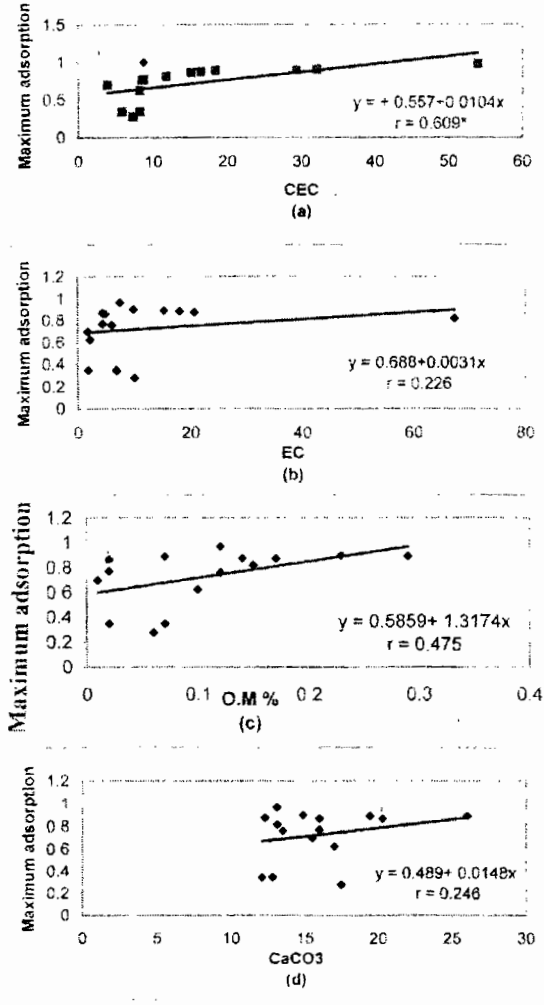
Concerning the relation between either clay as a mineral or $CaCO_3$ in the clay fraction, simple correlation coefficients were calculated between the adsorption maximum and total clay, clay as a mineral and $CaCO_3$ in the clay fraction (Figs 4-a,b,c). The obtained results showed positive linear relations between the aforementioned soil characters and the adsorption maximum, but the clay either as a total content or a clay mineral, was only significant as shown in the following equations, respectively:

Maximum adsorption = 0.5362 + 0.0119 total clay % r = 0.623*

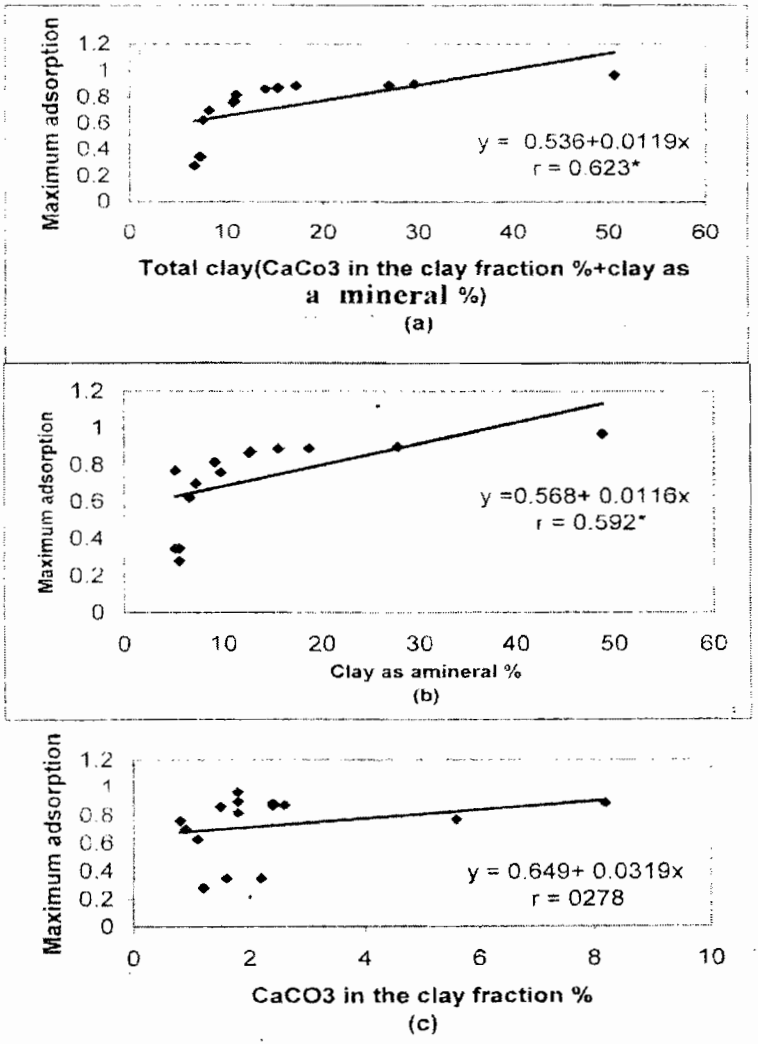
Maximum adsorption = 0.5683 + 0.0116 clay % as a mineral r = 0.592*

Maximum adsorption = 0.6496 + 0.0318 $CaCO_3$ % in the clay fraction r = 0.278

The insignificant correlation between the maximum adsorption and $CaCO_3$% in the clay fraction may be return to the low values of the finest clay fraction, which was not enough to be significant.



Figs. (3-a,b,c,d) The relationship between maximum adsorption and some chemical characteristics of studied soil samples.



Figs. (4-a,b,c) The relationship between maximum adsorption and some physical characteristics of studied soil samples.

In addition, multiple regression equations were statistically calculated to confirm the relationship between Zn reaction and soil characters as the following :

Maximum adsorption =0.499 + 0.123 clay % (as a clay mineral) + 0.140 $CaCO_3$% (in the clay fraction).

Maximum adsorption = 2.128 + 0.307 O.M% + 0.013 $CaCO_3$ % + 0.0004 EC_e + 0.009 CEC.

Harter and Naidu (2001) demonstrated that soils containing free $CaCO_3$ can sorb Zn and reduce its bio availability . It was found that calcite had a high affinity for Zn and gave a linear adsorption isotherm at low Zn concentration, while with higher Zn concentrations $ZnCO_3$ precipitation . The chemo sorption of Zn at low concentrations was considered to involve the replacement of Ca by Zn in the surface crystals of calcite. El Gabaly (1990) stated that montomoriullonite, specially at neutral or alkaline pH fixed Zn in amounts in excess of the CEC.

Not only, clay as a mineral absorbed Zn, but also $CaCO_3$ in the clay fraction (0.002 mm) also did . Numerous workers e.g. Mcbride 1994; Sparks 1995 and Harter and Naidu 2001, reported that Zn sorption in calcareous soils has been related to both nonspecific and specific interactions, involving both charged surfaces and neutral sites on mineral surfaces. The difference in charge between clay as mineral and $CaCO_3$ in the clay mineral (0.002 mm) may be affected the obtained statistically results.

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إدمصاص الزنك فى بعض أراضي توشكى

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الملخص العربى

أختبرت خمسة عشر عينة تربة من الطبقة السطحية لمواقع مختلفة فى منطقة توشكى تبعاً لمحتواها من كربونات الكالسيوم والطين بها ودراسة إدمصاص الزنك فى هذه الأرض البكر .

توافقت النتائج المتحصل عليها مع معادلة لانجومير خاصة عند التركيزات المنخفضة من الزنك والتى تراوحت قيمة السعة الأدمصاصية القصوى **adsorption maximum** بين ٢٧٨ .٠ ، ٩٦٩ .٠ ملليجرام زنك لكل جرام تربة وأرتبطت مع محتوى الطين الكلى ومعدن الطين بينما لم يوجد ارتباط معنوى بين الزنك وكربونات الكالسيوم فى قطر حبيبات الطين وأن كربونات الكالسيوم فى قطر حبيبات الطين قللت من تيسر الزنك ولكن القيم المتحصل عليها لم تكن احصائياً معنوية كما انه تراوحت قيم طاقة الارتباط **bonding energy** بين ٠,٠١٠ , ٠,٢١٦ لتر لكل ملليجرام تربة .